# Effect of Wastewater on the Concentrations of Mo, Zn, Cu, and Ni in Mill Creek at Marysville, Ohio[1]

TERESA M. MENSING AND GUNTER FAURE, Department of Geological Sciences, The Ohio State University at Marion, Marion, OH 43302 and Department of Geological Sciences, The Ohio State University, Columbus, OH 43210

ABSTRACT. **The presence of Zn, Cu, and Ni in solution in streams may be used to find deposits of the ore minerals of these metals in the Silurian carbonate rocks in northwestern and west-central Ohio. However, the concentrations of these metals in streams may be increased by discharge of municipal and industrial wastewater.**

**In the present study, a suite of water samples from Mill Creek in Union County, OH, was analyzed in order to determine to what extent wastewater discharged by the City of Marysville alters the chemical composition of the water. The data indicate that the concentrations of Na, K, and P increase significantly whereas those of Mg, Ca, Sr, and Ba decrease slightly. In addition, the concentrations of Mo, Zn, Cu, and Ni also rise, thereby changing the chemical signature of the water. The results demonstrate that the municipal wastewater of the City of Marysville is a significant source of transition metals in Mill Creek.**

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## INTRODUCTION

Effluent from municipal wastewater treatment plants in Ohio is discharged, in many cases, into nearby streams. This practice is monitored by the Environmental Protection Agency of Ohio and does not necessarily constitute a threat to human health (USEPA 1986). Nevertheless, the discharge of the effluent changes the chemical composition of the water in the streams by increasing the concentrations of metals such as Zn, Cu, and Ni (Sainey 1997). These metals as well as Pb are also released into groundwater by dissolution of certain ore minerals that occur in the Silurian dolomites of northwestern and west-central Ohio (Heyl and Brock 1962, Botoman and Faure 1976, Haden 1997). Therefore, the presence of these metals in streams of this area can be used to find metallic mineral deposits of potential economic value.

However, the release of municipal and industrial wastewater into the streams of northwestern and west-central Ohio makes it difficult to use the chemical composition of streams to locate significant deposits of sphalerite (ZnS) and other potentially valuable ore minerals in Ohio and Indiana (Shaffer 1981).

The objective of this study was to quantify the changes in the chemical composition of water in a small stream in west-central Ohio that result from discharge of effluent by a municipal wastewater treatment facility. For this reason, nine water samples were collected along the course of Mill Creek in order to document changes in their chemical composition that may be attributed to the discharge of wastewater by the City of Marysville, OH (Fig. 1).

Mill Creek arises near the village of Rushsylvania in Logan County, flows southeast for about 40 miles, and enters the Scioto River at Bellepoint in Delaware County, OH. Its average monthly discharge measured by the US Geological Survey from 1944 to 1993 about 1.5 miles upstream of Bellepoint ranges from 25.3 $ft^3$/sec in September to 342 $ft^3$/sec in March (Shindel and others 1994).

The concentration and isotope composition of strontium (Sr) in water collected close to the mouth of Mill Creek were first measured by Curtis and Stueber (1973) who reported a Sr concentration of 4 650 µg/L and an average $^{87}Sr/^{86}Sr$ ratio of 0.7080. Additional measurements of the concentrations of Sr in surface water and groundwater in the drainage basin of the Scioto River were published by Eastin and Faure (1970), Stueber and others (1972, 1975), and by Steele and Pushkar (1973). More recently, Hicks (1994) measured concentrations of the major cations (including Sr) of water collected along the course of the Scioto River and its major tributaries, but not including Mill Creek.

All of these studies have demonstrated that the water in the Scioto River and its western tributaries upstream of the glacial limit (located about 6 miles downstream from Chillicothe) have elevated Sr concentrations that exceed 1 000 µg/L in most cases. Feulner and Hubble (1960) attributed the Sr enrichment of ground and surface water of Champaign County in northwestern Ohio to the presence of celestite ($SrSO_4$) in the glacial deposits and bedrock of this area. Subsequently, Essenburg (1997) drew attention to the existence of a significant geochemical anomaly in northwestern Ohio based on high (Sr/Ca) ratios in surface waters where the concentration of Sr is expressed in µg/L and that of Ca in mg/L. The (Sr/Ca) ratios of Mill Creek range from 47.0 to 84.5 and are higher than those of all major rivers in Ohio.

## MATERIALS AND METHODS

Collection of water samples and interpretation of their chemical composition were carried out by the students enrolled in a course on Environmental Geology during the autumn quarter of 1995 at The Ohio State University at Marion. The student participants in this research project are identified in the Acknowledgment section of this report.

Water samples were collected on 30 September 1995

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from bridges at sites identified in Figure 1 and were stored in new 500-mL polyethylene bottles that were rinsed with the water being collected at each site. After filtering through 0.45 μm filters (Millipore Corp.) under vacuum in the laboratory, the samples were acidified to about pH 3 by the addition of 2 to 3 drops of concentrated reagent-grade nitric acid. The water samples were analyzed by XRAL Laboratories, Toronto, Ontario, by means of Inductively-Coupled Plasma Spectrometry (ICP).

## RESULTS

The results are listed in Table 1A and B together with the detection limits. Samples 8 and 9 (Fig. 1) are duplicates that were analyzed in order to test the reproducibility of the data reported by the analyst. The results demonstrate that the duplicate analyses in Table 1A (mg/L) differ by less than 1.0%, whereas the duplicate analyses in Table 1B (μg/L) differ by varying percent amounts from 0.12% (strontium) to 16% (zinc). The concentrations of the following elements were below the limit of detection expressed in parts per billion or μg/L indicated in parentheses: Be (<5 ppb), Al (<50 ppb), Sc (<1 ppb), Ti (<10 ppb), V (<10 ppb), Cr (<10 ppb), Co (<10 ppb), As (<30 ppb), Y (<5 ppb), Zr (<10 ppb), Ag (<1 ppb), and Cd (<10 ppb).

Concentrations of major cations in Mill Creek at sites 1 through 3, located upstream of the wastewater treatment plant in Marysville, varied only within narrow limits (Table 1A). Calcium was the most abundant cation with an average concentration of 93.1 ± 2.2 mg/L, followed by Mg (48.0 ± 1.2 mg/L), Na (20.9 ± 3.1 mg/L), Sr (5.08 ±

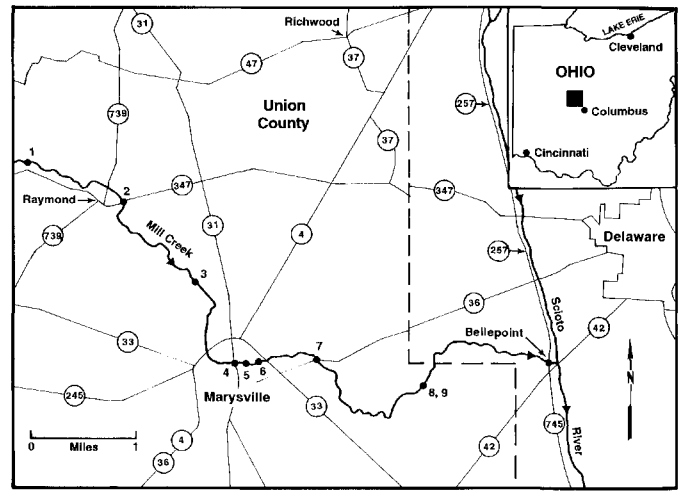


FIGURE 1. Map of parts of Union and Delaware counties in west-central Ohio showing the locations of collecting sites along Mill Creek.

TABLE 1A

*Concentrations of major cations in the water of Mill Creek in units of mg/L (ppm) at sites identified in Figure 1.*

| | 1 | 2 | 3 | 4 | 5[1] | 6 | 7 | 8[2] | 9 | Detection |
|---|---|---|---|---|---|---|---|---|---|---|
| Distance, miles | 0 | 1.11 | 2.47 | 3.66 | | 3.91 | 4.46 | 6.09 | 6.09 | limit |
| Na | 17.4 | 22.2 | 23.2 | 99.2 | 329 | 266 | 265 | 189 | 189 | 0.05 |
| Mg | 46.9 | 48.0 | 49.2 | 29.7 | 25.7 | 27.2 | 28.3 | 42.7 | 42.7 | 0.05 |
| K | 3.5 | 4.2 | 4.3 | 4.4 | 12.8 | 13.4 | 13.2 | 10.8 | 10.7 | 0.10 |
| Ca | 95.1 | 93.6 | 90.7 | 58.9 | 47.8 | 61.2 | 63.4 | 102 | 103 | 0.05 |
| Sr | 4.98 | 5.04 | 5.23 | 4.60 | 4.49 | 5.17 | 5.10 | 8.31 | 8.32 | 0.001 |

TABLE 1B

*Concentrations of minor cations in the water of Mill Creek in units of μg/L (ppb).*

| | 1 | 2 | 3 | 4 | 5[1] | 6 | 7 | 8[2] | 9 | Detection |
|---|---|---|---|---|---|---|---|---|---|---|
| Distance, miles | 0 | 1.11 | 2.47 | 3.66 | | 3.91 | 4.46 | 6.09 | 6.09 | limit |
| P | <50 | <50 | <50 | 164 | 6 470 | 4 650 | 4 540 | 2 380 | 2 340 | 50 |
| Mn | 8 | 12 | 6 | 17 | 20 | 58 | 28 | 8 | 9 | 5 |
| Fe | 65 | 61 | <50 | 58 | 103 | 178 | 159 | 80 | 88 | 50 |
| Ni | <10 | <10 | <10 | <10 | 35 | 29 | 28 | <10 | <10 | 10 |
| Cu | 20 | <5 | 6 | <5 | 41 | 10 | 8 | <5 | <5 | 5 |
| Zn | 13 | <5 | 6 | <5 | 77 | 55 | 43 | 25 | 21 | 5 |
| Mo | <10 | <10 | <10 | 11 | 215 | 172 | 143 | 136 | 132 | 10 |
| Ba | 72 | 62 | 62 | 29 | <10 | 15 | 24 | 40 | 39 | 10 |

[1]Sample 5 is water from the wastewater treatment plant in Marysville.
[2]Samples 8 and 9 were collected at the same site in order to check the reproducibility of the analyses.

0.13 mg/L), and K (4.00 ± 0.44 mg/L). These average concentrations are consistent with the Silurian limestones and dolomites that underlie the drainage basin of Mill Creek. Except for Ba, the concentrations of the trace metals at sites 1 to 3 are close to their respective limits of detection (Table 1B).

Sample 4, collected from the bridge on Rt 31 upstream of the wastewater treatment facility in Marysville (Fig. 1), had slightly elevated concentrations of Na (99.2 mg/L) and P (164 µg/L), but lower concentrations of Ca (58.9 mg/L), Mg (29.7 mg/L), Sr (4.60 mg/L), and Ba (29 µg/L) than samples 1 to 3 described above. The increased Na concentrations of sample 4 and the depression of the Ca concentrations in samples 4, 6, and 7 are illustrated in Figure 2.

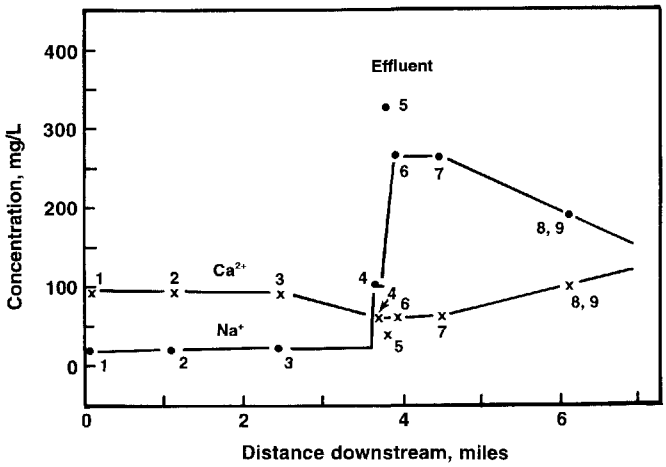


FIGURE 2. Variation of the concentrations of Na and Ca along the course of Mill Creek. The discharge of effluent (collecting site 5) increased the Na concentration but decreased the Ca concentration of the stream.

The wastewater (Sample 5) discharged into Mill Creek in Marysville had high concentrations of Na (329 mg/L), P (6 470 µg/L), and of the trace metals (Mo, Zn, Cu, Fe, and Mn) compared to samples 1 to 3 collected upstream of Marysville (Table 1A,B). The enrichment of the wastewater in these elements compared to water in Mill Creek is illustrated in Figure 3 in terms of the ratios of the concentration of an element in the wastewater divided by the average concentration of that element in samples 1 to 3 upstream of the City of Marysville. The results in Figure 3 demonstrate that the wastewater is strongly enriched in Na (15.7 times) and P (129.4 times) and that the concentrations of Fe, Mn, Ni, Cu, Zn, and Mo in the wastewater are higher than they were in Mill Creek water upstream of Marysville by factors that increase from Mn (2.30) to Mo (21.5). The enrichment factors of K, Mg, Ca, Sr, and Ba are less than 1.0.

## DISCUSSION

The elevated concentration of Na in the wastewater is primarily attributable to the use of water softeners and to the addition of table salt (NaCl) to human food (Hicks 1994). The P concentration of the wastewater is remarkably high in view of the reduction of the P content

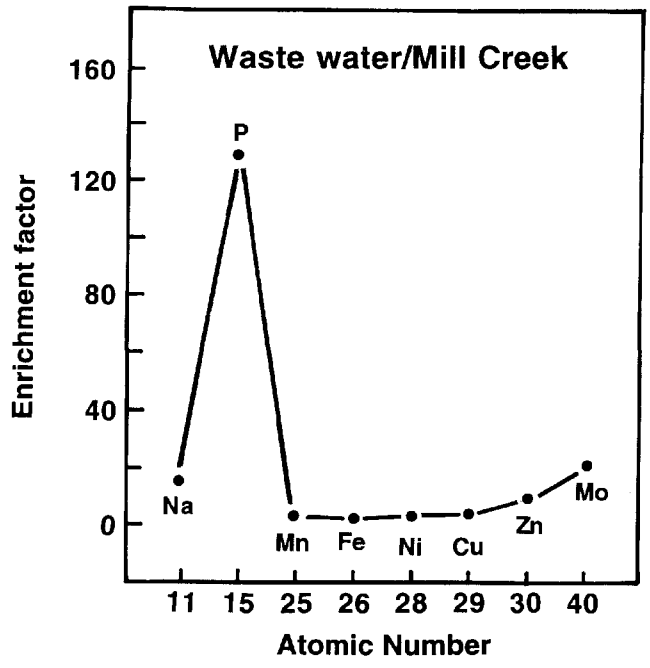


FIGURE 3. Comparison of the concentrations of selected elements in the wastewater (collecting site 5) and Mill Creek (collecting sites 1 to 3) by means of the enrichment factor calculated as the ratio of the concentration of an element in the wastewater divided by the average concentration of that element in samples 1 to 3 collected upstream of the City of Marysville.

of household detergents from about 12% in the 1980s to about 2.5% at the present time. However, detergents used in hospitals, for food preparation, and in dishwashers still have high P concentrations (Terry J. Logan, personal communication, 22 June 1998). Therefore, the high P concentration of the wastewater probably originates from the use of detergents although organic waste may also contribute. The P content of the wastewater is not attributable to effluent discharged by the Scotts Fertilizer Company in Marysville because that firm was not connected to the municipal sewer lines in the fall of 1995 when the samples for this study were collected.

The trace metals (Mo, Zn, Cu, Ni, Fe, and Mn) in the wastewater may have a variety of sources, including corrosion of metal pipes in municipal and domestic plumbing systems (Fe, Mn, Cu), use of galvanized kitchenware and Zn-bearing solder (Zn), and handling of coins (Cu, Ni). However, the elevated concentration of Mo in the wastewater is not explained by these sources.

The evidence presented in Table 1B and Figure 3 clearly demonstrates that the wastewater discharged into Mill Creek by the Marysville treatment plant on 30 September 1995 increased the concentrations of Mo, Zn, Cu, and Ni and thereby altered the chemical signature of that stream. The chemical profile in Figure 4 indicates that the concentrations of Mo and Zn rose abruptly at the point of discharge of the wastewater in Marysville and then gradually decreased downstream until Mill Creek emptied into the Scioto River. The concentrations of Ni and Cu vary similarly but are not shown in Figure 4.

The pattern of variation of the concentrations of Mo and Zn along the course of Mill Creek in Figure 4 indicates

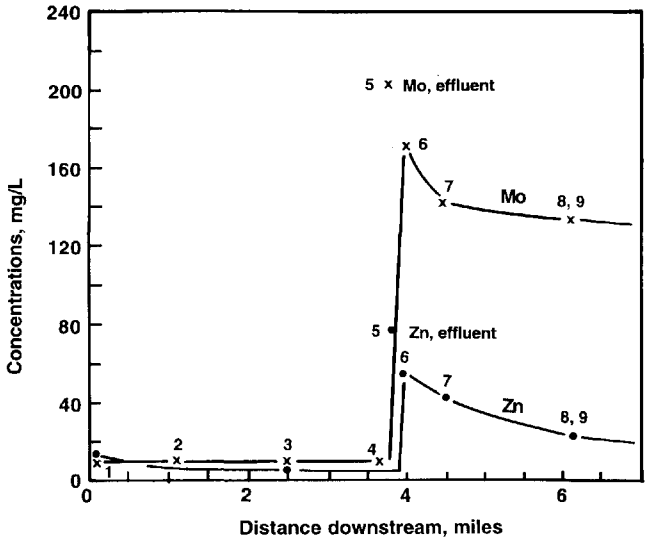


FIGURE 4. Variation of the concentrations of Mo and Zn along the course of Mill Creek. The discharge of the effluent (collecting site 5) increased the concentrations of both elements in the water of Mill Creek.

that the wastewater discharged at Marysville acts as a point source for these metals. Similarly, the concentrations of Na (Fig. 2), K, and P are strongly affected by the input of the wastewater (Table 1A,B). In contrast, the small variations of the concentrations of the alkaline earth elements (Mg, Ca, Sr, and Ba) probably reflect the entry of water from small tributaries and groundwater into Mill Creek.

Although these conclusions apply strictly to conditions in Mill Creek on the day the samples were collected, Piatak (1988) reported that on 1 October 1997 the concentrations of Na, P, K, Mo, Ni, and Zn in Nettle Creek all increased in the immediate vicinity of Millerstown, Champaign County, in west-central Ohio. These results therefore demonstrate that the contamination of Mill Creek by wastewater is not an isolated incident.

## CONCLUSION

The concentrations of Na, K, P, Mo, Zn, Ni, Cu, and Fe of Mill Creek increase at the discharge point of wastewater in Marysville, OH, whereas those of Mg, Ca, Sr, and Ba remain virtually unaffected. The enrichment of the water of Mill Creek in Mo, Zn, Cu, and Ni by the wastewater alters its chemical signature and limits its use for geochemical exploration of the bedrock underlying this drainage basin.

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